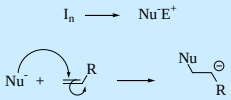
Anionic Polymerization

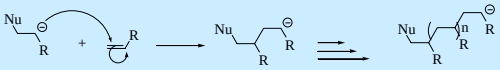
Concepts

General Mechanism

Initiation



Propagation



Reaction is facilitated by electron withdrawing groups, e.g. :

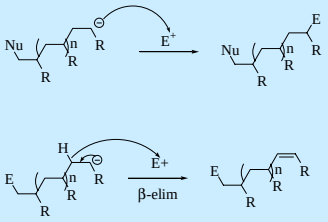
NO_2, CN, CO_2R, $CH{=}CH_2$, Aryl

Anionic Polymerization

Concepts

General Mechanism

Termination



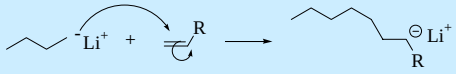
Anionic Polymerization

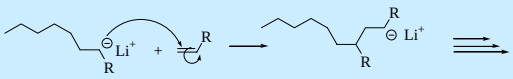
Chemistry

Initiators

1. Nucleophilic: Strength of nucleophilic initiater depends on monomer

n-C_4H_9Li, ArylMgBr, RO^-, CN^-, NaNH2, $LiNR_2$, RNH_2



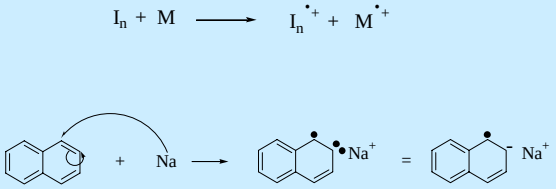


Anionic Polymerization

Chemistry

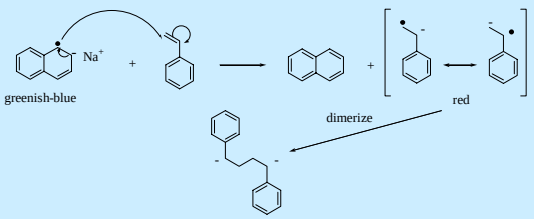
Initiators

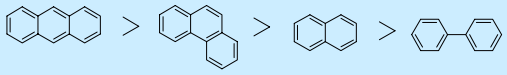
2. Electron Transfer



Anionic Polymerization

Chemistry



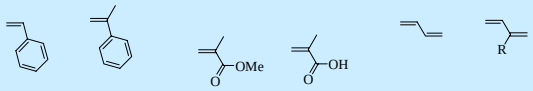


Anionic Polymerization

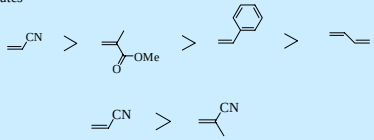
Chemistry

Propagation

Monomer Structure: anion stabilized by electron withdrawing group



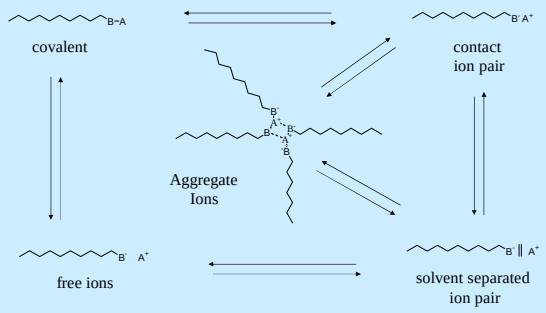
Rates



Rate determined by both sterics and polar factors. Trend is not the same as free radical

Chemistry — Anionic Polymerization

Ion Structure: Species



Chemistry — Anionic Polymerization

Counterions

Counterion	Rate in Dioxane (less polar)
Li^+	0.94
Na^+	3.4
K^+	19.8
Rb^+	21.5
Cs^+	24.5
Solvation not important in dioxane, therefore, the ion pair with the highest	Reactivity is that with the weakest bond (releases more highly active free ions)

Chemistry — Anionic Polymerization

Solvent Effects

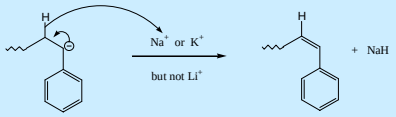
Solvent	Dielectric Constant	k_p^{app}
Benzene	2.2	2
Dioxane	2.2	5
THF	7.6	550
1,2 Dimethoxyethane	5.5	3800

Anionic Polymerization

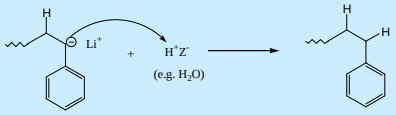
Chemistry

Termination

1. Hydride Transfer



2. Chain Transfer or Protonating Impurities

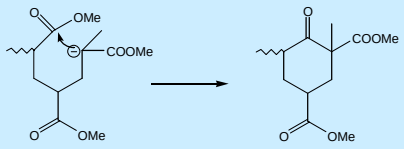


Anionic Polymerization

Chemistry

Termination

3. Intramolecular



Anionic Polymerization

Kinetics

Dissociation: e.g. free ions

$$Nu^- E^+ \rightleftharpoons Nu^- + E^+ \qquad R_d = k_d [Nu^- E^+]$$

Initiation $\qquad R_i = k_i [M] [Nu^-]$

$$K = \frac{[Nu^-][E^+]}{[Nu^- E^+]} \longrightarrow [Nu^-] = \frac{K [Nu^- E^+]}{[E^+]}$$

$$R_i = \frac{k_i K [Nu^- E^+] [M]}{[E^+]}$$

Anionic Polymerization

Kinetics

Propagation $[NuM^-] + [M] \longrightarrow [NuMM^-]$

$$R_p = k_p [M] [NuM^-]$$

Termination: $[NuM^-] + [H_2O] \longrightarrow [NuMH] + OH^-$

$$R_t = k_t [H_2O] [NuM^-]$$

Steady state approx:

$$R_i = \frac{k_i K [Nu^- E^+] [M]}{[E^+]} = R_t = k_t [H_2O] [NuM^-]$$

$$[NuM^-] = \frac{k_i K [Nu^- E^+] [M]}{k_t [H_2O] [E^+]}$$

Anionic Polymerization

Kinetics

$$R_p = k_p [M] [NuM^-]$$

$$R_p = \frac{k_p k_i K [Nu^- E^+] [M]^2}{k_t [H_2O] [E^+]}$$

Degree of Polymerization $DP = R_p/R_t = R_p/Ri$

$$= \frac{k_p k_i K [Nu^- E^+] [M]^2}{k_t [H_2O] [E^+]} \Big/ \frac{k_i K [Nu^- E^+] [M]}{[E^+]}$$

$$= \frac{k_p [M]}{k_i [H_2O]}$$

Note: = [M] / [I] or 2[M] / [I]

Anionic Polymerization

Telechelic Transformations

Block Copolymers

$$\sim\sim AAA^- \xrightarrow{B} \sim\sim AAABBB^- \xrightarrow{C} \sim\sim AAABBBCCC^-$$

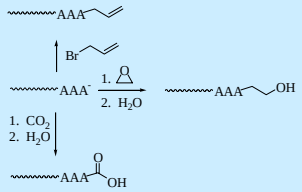
Reverse Transformation

$$\sim\sim AAA^- \xrightarrow{COCl_2} \sim\sim AAA\text{-}C(=O)Cl \xrightarrow{AgSbF_6} \sim\sim AAA^+ SbF_6^- \xrightarrow{B} \sim\sim AAABBB^+ SbF_6^-$$

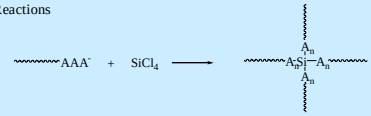
Anionic Polymerization

Telechelic Transformations

Synthetic Transformations



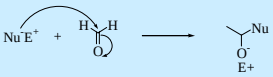
Coupling Reactions



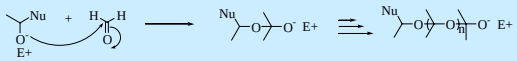
Anionic Polymerization

Carbonyl Polymerization

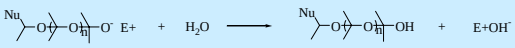
Initiation



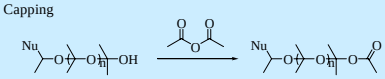
Propagation



Termination

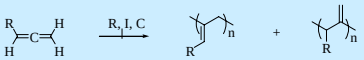


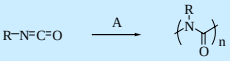
End Capping

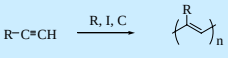


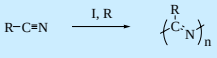
Anionic Polymerization

Other Anionic Polymerizations





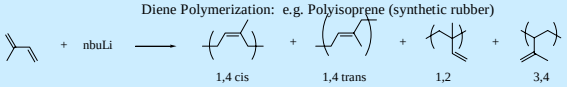




Anionic Polymerization

Stereochemical Considerations

Diene Polymerization: e.g. Polyisoprene (synthetic rubber)

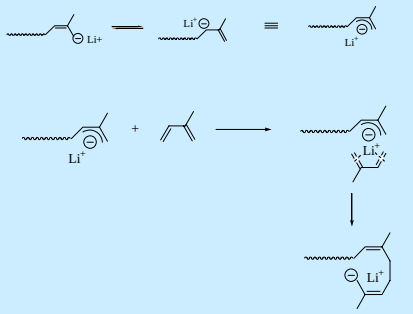


1,4 cis 1,4 trans 1,2 3,4

Counterion	Solvent	1,4 cis	1,4 trans	1,2	3,4
Li	Pentane	94	---	---	6
Li	Pentane/THF	0	25	10	65
Li	THF	---	---	25	75
Li	Et_2O	---	50	5	45
Na	pentane	small	40	7	53
K	pentane	small	55	7	38

Anionic Polymerization

Stereochemical Considerations



Note: Na^+ or K^+ not effective—too large to promote cyclic transition state